REMARKS

Further and favorable reconsideration is respectfully requested in view of the foregoing amendments and following remarks.

Thus, claim 1 has been amended to incorporate the subject matter of claim 6, as a result of which claim 6 has been cancelled.

Amended claim 1 also recites that the stretching step provides a stretched resin laminate with a reduced haze of at most 10%, which is based on the disclosure at page 11, lines 22-25 of the specification.

The patentability of the presently claimed invention over the disclosures of the references relied upon by the Examiner in rejecting the claims will be apparent upon consideration of the following remarks.

Thus, the rejection of claims 1-8 under 35 U.S.C. 103(a) as being unpatentable over Kawakami et al. (US '639) in view of Shiiki et al. (US '437) is respectfully traversed.

The present invention is based on the discovery of an unexpected effect of crystal stretching of a polyglycolic acid (PGA) resin layer in a multilayer resin laminate, as described at page 3, line 16 to page 4, line 10 of the specification.

Kawakami et al., at column 4, lines 15 - 25, discloses a process for producing a stretched PGA film including steps of melt-extruding a PGA material, quenching the extrudate and stretching the extrudate in a temperature range of from Tg (glass transition temperature) to Tm (melting point) of the PGA material. However, Kawakami et al. fail to teach or suggest a positive effect of the crystallization before the stretching of PGA resin, which has never been known before the present invention.

As described at page 4, lines 15 - 17 of "polymers.htm" cited in the Official Action, "Increased crystallinity is associated with an increase in rigidity, tensile strength and opacity (due to light scattering). Amorphous polymers are usually less rigid, weaker and more easily deformed. They are often transparent."

Additional differences between amorphous polymers and crystalline polymers are discussed in Encyclopedia of Polymer Science and Engineering, Volume 7, pages 88-106 (1987), a copy of which is enclosed. The differences between amorphous polymers and crystalline

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polymers are discussed at page 88 under the heading of "Crystallinity", and regarding behaviors in stretching at page 97, below Fig. 9.

The quenching step in Kawakami et al. is a step of retaining an amorphous state of the PGA resin by preventing crystallization due to remaining heat of the melt-extrusion. Before the present invention, including Kawakami et al., it had been conventional to minimize the crystallization of PGA resin before the stretching thereof since it results in a reduced stretchability (deformability) and opacification of the PGA resin. According to the present invention, however, it has been found that the crystallization before the stretching rather favors smooth stretching of the resin laminate including a PGA resin layer, and the adverse effect thereof of whitening can be avoided by re-arrangement of molecular chains during the crystal stretching, thus not leaving an obstacle to formation of a transparent stretched laminate film as described at page 3, line 16 to page 4, line 10 of the specification.

Regarding claim 2, the Examiner cites column 8, line 25 of Kawakami et al. which relates to transparency of the product film, whereas claim 2 relates to a haze value after cooling, i.e., before the reheating and stretching. Kawakami et al. aim at providing a transparent film after the stretching, and do not teach or suggest the positive effect of crystallization before the stretching which changes the transparent quenched PGA extrudate to be opaque. Accordingly, the opacification up to a haze of at least 40% by re-heating before the stretching is not an optimization suggested by any prior art including Kawakami et al., contrary to the Examiner's statement regarding claim 6.

Shiiki et al. has been cited as teaching the incorporation of a layer of PGA into a laminate sheet. However, the reference also does not teach or suggest the positive effect of crystal stretching of a PGA resin layer in a laminate resin sheet, thus failing to remedy the deficiency of Kawakami et al.

For these reasons, Applicants take the position that the presently claimed invention is clearly patentable over the applied references.

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Therefore, in view of the foregoing amendments and remarks, it is submitted that the ground of rejection set forth by the Examiner has been overcome, and that the application is in condition for allowance. Such allowance is solicited.

Respectfully submitted,

Kazuyuki YAMANE et al.

By _____
Michael R. Davis
Registration No. 25,134
Attorney for Applicants

MRD/cbc
Washington, D.C. 20005-1503
Telephone (202) 721-8200
Facsimile (202) 721-8250
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Fibers, Optical
to
Hydrogenation

CONTENTS

FILMS, MANUFACTURE

Virtually every thermoplastic can be used in film form. Most thermoplastic films are prepared by conventional extrusion techniques based on calendering or solvent casting or blown-film or tenter-film systems. In the selection of a film for a particular application, the properties of the thermoplastic materials must be considered in view of the application. Thermal properties, molecular characteristics, and crystallinity of the polymer affect processing and film properties. Additives influence extrusion and orientation processes and improve film properties.

Polymer Properties

Molecular Weight and Molecular Weight Distribution. Molecular weight and molecular weight distribution affect extrusion and orientation processes (qv) and the physical properties of the film, eg, tensile strength, elongation, impact resistance (qv), and optics.

Films prepared from high molecular weight materials exhibit mechanical strength, impact strength, and orientability. As molecular weight increases, melt strength increases. Tubular orientation requires high molecular weight and a melt index (MI) of 0.1–3 (ASTM D 1238 E) to provide adequate melt strength during extrusion and orientation. However, high molecular weight impedes processing and results in a film with poor optical clarity, despite orientation. Films of lower molecular weight material are brittle, difficult to orient, and have lower melt strength. Low molecular weight resins are characterized by good clarity and high extrusion or processing rates. Resins of low molecular weight with a melt flow (MF) of 6–12 (ASTM D 1238 E) are used for sheet casting because melt strength is not required but good clarity is of prime importance. For tenter-process extrusion, polymers of a middle range are employed, eg, polypropylene (PP) with MF 3–7 (ASTM D 1238 L), because melt strength is less critical. This is also true of tubular-film processes that employ an initial quenching step.

At the same molecular weight, optics, drawdown, and impact strength increase as molecular weight distribution narrows, whereas melt strength, die swell, shrinkage, and processibility decrease.

Crystallinity. The properties of a material are determined by its molecular structure; bulk properties are controlled by the spatial arrangement of the molecules. Polycrystalline materials are best understood in terms of a two-phase model consisting of amorphous and crystalline domains (1). The properties of each phase differ. The observed properties of a material depend on the component-phase properties and the interaction of the two phases. Structural parameters are determined by the ratio of the two phases and the average orientation of the molecules in each phase (2).

Increasing crystallinity of a polycrystalline polymer is accompanied by increases in modulus, stiffness, density, yield stress, chemical resistance, melting point, glass-transition temperature, abrasion resistance, creep resistance, and dimensional stability, and by reduction in impact resistance, elongation, thermal expansion, permeability, and swelling.

Final crystallinity and crystalline- and amorphous-phase orientation depend strongly upon process conditions.

Thermal Properties. The chemical nature of the polymer determines its stability to temperature, light, water, and solvents. Polymer chains form ordered structures, and the thermodynamics of this ordered state determines melting point T_m, the glass-transition temperature T_g, and mechanical and electrical properties. Thermal properties (qv) of film polymers are given in Table 1 (3–9). The polymers best suited for films have a glass-transition temperature below 0°C, a melting point above 100°C, and a decomposition temperature at least 50°C above the melting point. Such polymers, eg, polyethylene (PE), PP, and polystyrene (PS), can be extruded in conventional extruders.

Table 1. Thermal Properties of Film Polymers[a]

Class	Polymer	Common symbol	Glass-transition temp T_g, °C	Melting temp T_m, °C	T_{dec},[b] °C
polyolefin	high density polyethylene	HDPE	-(120–140)	130–137	335–450
	low density polyethylene	LDPE	-(95–130)	105–115	335–450
	polypropylene	PP	-10	170	328–410
	ethylene–propylene copolymer	EP	-30	128–145	328–410
	poly(1-butene)	PB	-24	126	288–425
	poly(4-methyl-pentene)	TPX	30	235	335
	polytetrafluoroethylene	PTFE	27	330	508–538
vinyl polymers	polystyrene	PS	85–105	240	285–440
	poly(vinyl acetate)	PVAC	75–105	240	213–325
	poly(vinyl chloride)	PVC	75–105	212–310	200–300
	poly(vinylidene chloride)	PVDC	-18	210	225–275
	poly(vinyl fluoride)	PVF	40	200–235	372–480
	polyacrylonitrile	PAN	97	320	250–280
	poly(methyl methacrylate)	PMMA	65	160	170–300
polyethers	polyoxymethylene	POM	-(65–110)	181	100
	poly(phenylene sulfone)		220	300	310
	cellulose triacetate	LA	105	306	250–310
polyesters	poly(ethylene terephthalate)	PET	81	265	283–306
	polycarbonate	PC	147	225	420–620
polyamides	polycaprolactam[c]		40–87	220	310–380
	poly(hexamethyleneadipamide)[d]		50	265	310–380
	polyundecanoamide[e]		46	194	310–380
	polyimide		310–365		310–380

[a] Temperature quoted represents values for specific grades of commercial materials and may not be representative of all materials of this classification.
[b] Decomposition temperature.
[c] Nylon-6.
[d] Nylon-6,6.
[e] Nylon-11.

When the melting temperature is too close to the decomposition temperature, a film can be produced by solvent casting or reduction of the melting point by copolymerization (10). This reduces the crystalline order of the polymer and lowers the energy required for melting. In addition, the decomposition rate can be lowered by heat stabilizers. Extruder and die are designed with flow lines to avoid melt stagnation and push the polymer through extruder and die as quickly as possible. A lubricating additive minimizes melt sticking on the metal surface. Unplasticized PVC, polyamides, and polyesters are extruded in this way (11).

When the melting temperature is above the decomposition temperature, as with cellulose or polyacrylonitrile, solvent casting and coagulation are used.

When no solvent is convenient and the use temperature of the film is below the T_g of the polymer, a nonvolatile liquid is required, which acts as solvent at high temperatures and as plasticizer at room temperature; both T_g and the melting temperature are reduced. Poly(vinyl chloride) (PVC) plasticized with phthalates up to half its weight (11) can be extruded, as can vinylidene chloride–vinyl chloride copolymer.

Additives. Organic and inorganic additives or coatings impart the functionality to the finished product demanded by the consumer (7,12–14) (see Table 2). Additives must conform to government regulations on material handling and health hazards for both workers and consumers.

Stabilizers reduce degradation (qv) during processing to lower molecular weight polymers resulting in poor film properties, gels, and discoloration. Hindered phenol antioxidants (qv) combined with phosphites reduce thermal degradation of polyolefins. Other stabilizers improve long-term stability to heat and light.

Friction can be overcome by slip agents such as saturated and unsaturated fatty acid amides. These agents migrate to the film surface during processing and upon aging at elevated temperature. Concentrations depend upon film thickness, processing parameters, and residence time at elevated temperatures.

Antiblock agents are typically used to prevent adherence, ie, blocking, of two film surfaces. They are small particle-size fillers affecting surface smoothness without reducing clarity.

Antistatic agents (qv), typically amine derivatives of glycerol monostearate, are primarily used to reduce static generation in packaging equipment and enhance shelf life. These additives are particularly effective for films designed for packaging powders.

Rheology. The viscous and elastic behavior of melts determines the design of extruder screws, melt pipes, filters, and die configuration. The elastic nature of the melt at any temperature affects surface smoothness, layer thickness, and stability. Solid-phase rheology influences stretching, such as occurs in the stepwise or simultaneous biaxial orientation. The rheology of the finished product also determines film behavior on packaging machines, printing presses, or laminators where the film is both heated and loaded by tension changes (12,13) (see also RHEOLOGY; DIE DESIGN; SCREW DESIGN).

Manufacturing Processes

Extrusion

Extrusion (qv) is widely used for the manufacture of polymeric films because it permits the preparation of highly uniform polymer melts at high rates (15–18). An extruder (Fig. 1) consists of a hollow cylindrical barrel fitted with external heaters. The inner surface is coated with a hard metal liner such as Xalloy. A screw is fitted into this cylinder with a specific geometry determined by the polymer and the desired thermal condition of the melt. The screw is driven by

Table 2. Film Additives

Additive function	Supplier	Trade name	Chemical name or class
antioxidants	Goodrich	Goodrite 3114	phenolic
	Koppers	BHT	butylated hydroxytoluene
	Koppers	DBPC	di-tert-butyl-p-cresol
	Mobil		trialkylhydrogen phosphites
	Mobil		dialkylhydrogen phosphites
	CIBA-GEIGY	Irganox	high molecular weight hindered phenols
	Cardinal	Poly TDP-2000	hydroquinone derivative
heat stabilizers		CC-7711	organotin
	American Cyanamid	Cyastab	lead-based carbonates, sulfates, phthalates phosphites
	Ferro		barium–cadmium
			cadmium–zinc
	Dart and Kraft		antimony mercaptides
	Uniroyal Chemical		N,N'-diphenyl-p-phenylene diamine
uv stabilizers	American Cyanamid	Cyasorb	benzophenone
			benzotriazole
	Borg-Warner	Spinuvex	hindered amine (HALS)*
	Borg-Warner	Weston 619	solid phosphite
	CIBA-GEIGY	Tinuvin	hindered amine (HALS)*
slip agents	Witco	Kenamide	fatty acid amides
	Dow Corning	Dow 200 fluid	polydimethylsiloxane
	Allied	A-C Polyethylene	PE wax
		Admer	polyolefin
fillers, antiblock agents		Alumite	calcium carbonate
	North Georgia Minerals & Chemicals	DiCaperl Hp-510	glass bubble
			aluminum trihydrate
			celestite
			barytes
			talc
	James River	Solka-Floc	cellulose
	Manville	Celite	diatomaceous earth
	Manville	Micro-Cel	hydrous calcium silicate
		Suzorite	mica
		Wollastonite	calcium m-silicate
		Glomax	calcined kaolin clay
		Kaopaque	delaminated aluminum silicate

* HALS = Hindered amine light stabilizer.

an electric motor through a gear reducer sized for the speed and power requirements of the screw. The typical barrier screw shown in Figure 2 takes advantage of the melting mechanism in the extruder to increase efficiency. Most of the energy required to melt the polymer is supplied by the motor. Barrel temperature is maintained by electric heaters, which often contain channels for cooling water.

The solid polymer is introduced into the feed throat of the extruder and conveyed into the screw by its turning motion (15). It is compacted into a solid
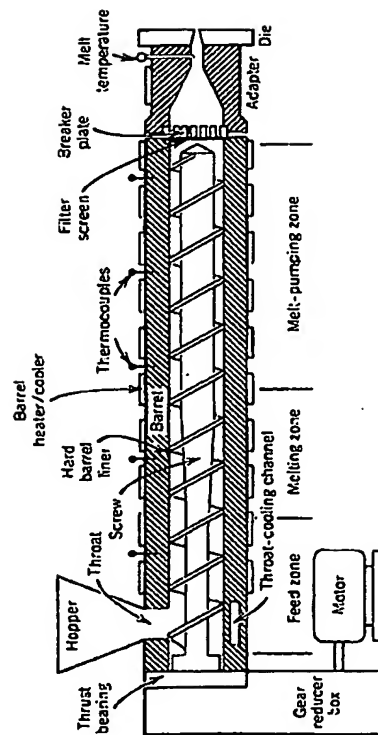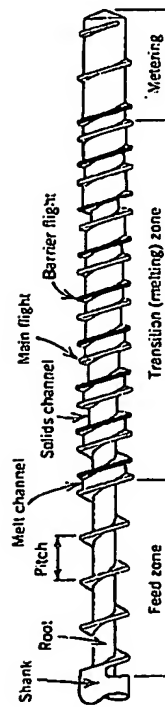
Fig. 1.   Extruder.

Fig. 2.   Barrier flight screw.

plug, which is melted by contact with the hot barrel. Molten polymer is collected by the screw flights and pumped toward the end of the extruder. At the end of the screw, the polymer is completely melted. The melt is mixed by rotating the screw, which generates enough pressure to push the melt through a die and to the next step (19,20). The condition or quality of the melt is extremely important for film quality and the stability of the process. The extrusion conditions affect crystallization behavior and molecular weight of the film.

The melt is produced by the viscous dissipation of mechanical energy into a very thin layer of molten polymer located between the compressed solid plug and the heated barrel surface (16) (Fig. 3). Owing to the high viscosity of the polymer melt, typically 50–1,000 Pa·s (500–10,000 P), large amounts of energy are dissipated in the melt as the motor turns the screw. The energy is converted into heat, which is transferred to the solid polymer and the barrel, raising the temperature of the melt. Excessive temperatures or mechanical work can cause thermal, oxidative, or mechanical degradation of the polymer.

The polymer melt flows through a die to the next process step; flat, circular, or slot dies are preferred. The flow through the die must be uniform across the exit plane. However, this is complicated by the nonlinear dependence of melt viscosity on both temperature and shear rate in the die (19,20). The suitability
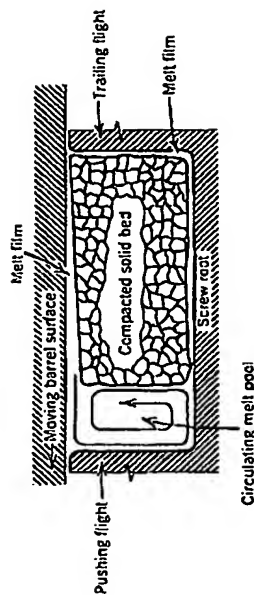
Fig. 3.   Melting mechanism of single-screw extruders.

of a material is determined by measuring the flow properties with a capillary rheometer in the temperature and shear-rate range expected. Melt elasticity can cause flow instabilities, which affect haze and thickness (21,22) or the operation of downstream equipment. Exit velocity, flow characteristics, and quenching rate may impart significant orientation to the polymer. In some instances, melt orientation is reduced; in others, it is maintained by quenching.

In flat-die extruders, slot and coat-hanger die geometries (Fig. 4) predominate, whereas in circular-die extruders, spiral dies (Fig. 5) predominate. A die is usually constructed of tool steel and heated to maintain the desired temperature for optimum flow; temperature control is very important. A uniform flow through the die is determined by the design of the internal distribution manifold. For good melt distribution, this section must be designed to maintain uniform flow rate, pressure drop, and shear (20). Independent flow adjustment is usually provided by an adjustable die lip or choker bar. These devices ensure a uniform flow by selectively changing the shear rate of the melt before it leaves the die. Multiple temperature zones, standard on most dies, permit the selective alteration of the temperature across the die face, ensuring production of a flat sheet. This is necessary to counteract gauge variations caused by possible nonhomogeneous melt from the extruder, inadequacies in the die design, and the physical limitations imposed in the machining of the internal configuration of the dies.
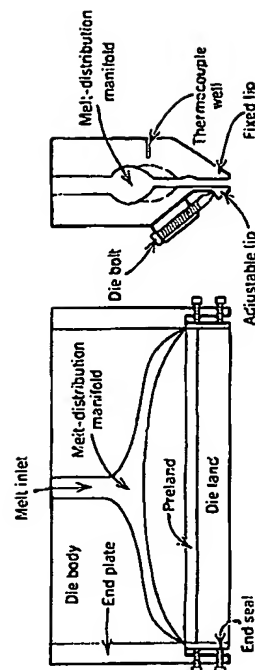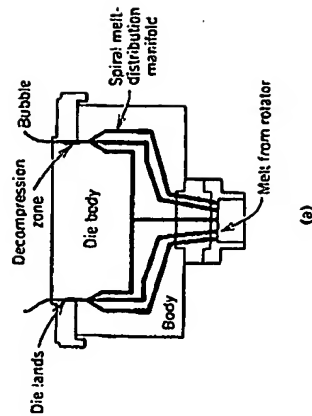

Fig. 4.   Coat-hanger die.

Fig. 5. (a) Tubular (three-layer) spiral die; (b) detail of spiral melt manifold.

To ensure isothermal flow, die temperatures are maintained as close to the melt temperature as is practical. Die gaps vary, depending upon the speed with which material is removed from the die lips, as this determines the shear rate. This is important because of die swell and melt fracture. Die gap also determines the final film thickness. Die gaps are 0.25–2.5 μm, small compared with the typical die width of 39–305 cm.

Coextrusion. Coextrusion technology has been developed in conjunction with new polymers providing the film structures required for flexible packaging (see FILMS, MULTILAYER). Coextrusion is the most economical method of combining films into functional multilayer packaging.

Multiple melt streams from several extruders are combined either in a feed block (Fig. 6) or a multiple-cavity die (Fig. 7), resulting in a stratified flow from the die. Feed blocks may be used in conjunction with a multiple-cavity die or to produce structures with many layers. The latter are used for films requiring several layers to improve adhesion between the several polymers.

Coextrusion is promoted by the laminar flow of the melt in the feed block and die, which prevents the mixing of the various layers. The laminar flow is due to the low Reynolds numbers (low inertia between flow planes) that result
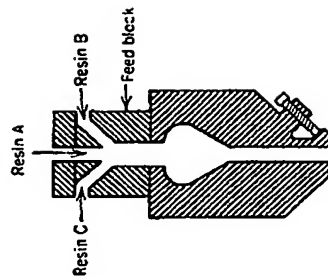
Fig. 6. Coextrusion system (single-cavity die) using a feed block for three polymer streams.
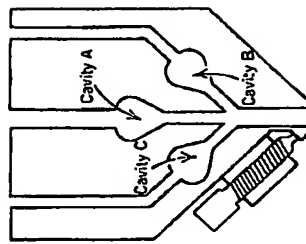

Fig. 7. Multicavity coextrusion die with multiple melt-distribution manifolds.

from the high melt viscosities (19,20). However, the generation of interfaces between the flowing materials requires that melt viscosities between the layers are sufficiently matched to prevent flow instabilities (23). Therefore, coextrusion requires superior equipment and control throughout.

In another method, two or three melt streams from separate extruders can be combined and cast to form a multilayer structure. Alternatively, a melt stream and a quenched uniaxially oriented web are combined on a chilled drum, providing the web with functionality; this method is known as the extrusion coating process (12).

Casting. In casting (qv), a self-supporting sheet is formed from a melt supplied by an extrusion system. Processing conditions have a profound effect on sheet properties and subsequent operations. Depending on the polymer, the rate of heat removal determines the extent and morphology of crystallinity of the sheet and the degree of residual orientation. Also important is the temperature at which the heat is removed from the sheet. Thus, heat-transfer analysis of casting processes is essential for the design of an efficient system.

Quenching is a continuous operation and must be regarded as an unsteady state. It can take place in water, on a continuous steel band, on a casting drum, or by a combination of these methods (see Fig. 8). The heat-transfer analyses for these systems are similar, differing primarily in the magnitude of heat-transfer coefficients. Heat-transfer rate, heat-transfer temperature, melt temperature, and crystallization kinetics determine the optimum quenching conditions. The cast sheet must be strong enough to be transported to the next stage of the manufacturing process.
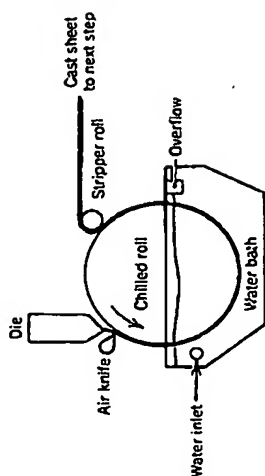

Fig. 8.   Water bath–chill roll quenching system.

If a high quality surface or a uniform heat-transfer rate is required, a pinning step may be needed. Pinning is defined as the forcible application of the molten film to the cold casting surface. It may be carried out by an air knife, a vacuum box, a nip roll, or a strong electrostatic field. Pinning is needed for high production rates while maintaining uniform properties across the quenched web. The pinning force prevents air from being trapped between the film and the casting surface. It depends upon the speed of the operation and the quality of the sheet required for the particular product to ensure intimate contact with the surface against which the polymer is being solidified.

Examples of cast films are high clarity low density polyethylene (LDPE) film for bread bags, pallet wraps, PVC sheets, and polycarbonate (PC) or acrylic sheets for glazing applications. Casting is the initial step in the production of biaxially oriented PP, PS, and poly(ethylene terephthalate) (PET) films.

Uniaxial Orientation.   Uniaxial orientation enhances the physical properties of sheets and films in one direction; properties in the perpendicular direction are usually far inferior (23). The orientation temperature, governed by the material, determines the final properties. Semicrystalline polymers are oriented between the glass-transition temperature T_g and the melting point T_m, whereas amorphous polymers are oriented above T_g. In general, the polymer is oriented by rapid stretching in the temperature ranges described above, followed by rapid quenching. The latter ensures that the orientation is not lost by molecular relaxation. The degree of orientation is determined by the extension rate and the degree of extension (2). A wide variety of commercial equipment is available for uniaxial orientation, as well as proprietary equipment developed for special processes or high production rates. Orientation (qv) is a continuous operation and

occurs in the direction of film motion or the machine direction (MD). Usually, a cast sheet is transported on heated rollers (Fig. 9) to permit the sheet to reach a uniform temperature at which the polymer molecules are sufficiently mobile. Having reached this temperature, the sheet is abruptly accelerated between two rollers of different speeds. This point is defined as the draw point. In some instances, additional heat may be required to boost the temperature, or nip rolls are needed to regulate tension and prevent film slippage. Uniaxial film can be obtained by orienting perpendicular (transverse) to the machine direction using tenter frames or melt inflation where the removal rate is equal to the melt velocity at the die. However, these two methods are seldom employed. The properties required by the user determine the orientation required to develop the desired physical properties.
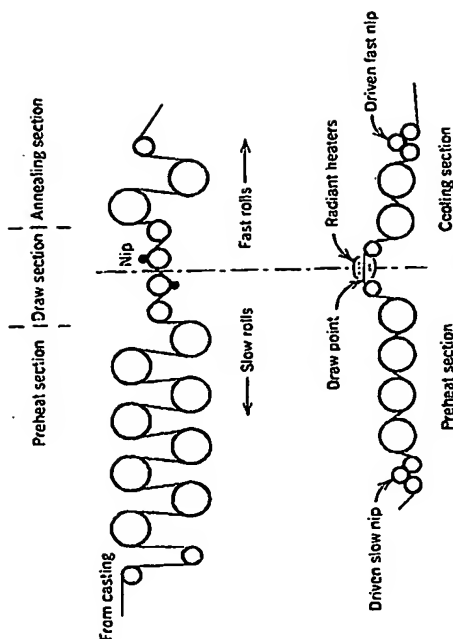

Fig. 9.   Machine-direction (MD) orientation.

Amorphous and semicrystalline polymers behave very differently when subjected to uniaxial orientation. Amorphous polymers may be drawn to any extent or thickness if properly supported, whereas semicrystalline polymers show distinct and abrupt thickness changes, ie, necking, when drawn (2). Necking may limit the rate at which the polymer is drawn because of the heat generated in the neck region. The heat generated can be high enough to cause chain scission resulting in breakage of the sheet at the draw point (24). Necking serves to define a minimum draw ratio for the material at the temperature and draw rate employed.

The relationships between physical properties and molecular orientation of uniaxial products are well understood for both amorphous and semicrystalline polymers (25). The principal change that occurs upon orientation is the preferential alignment of the c-axis of molecular chains in the direction of the orientation in the amorphous and crystalline phases of semicrystalline polymers (26,27). The preferred c-axis orientation allows the strong covalent bonds along the chain

backbone to carry loads applied in the orientation direction. Perpendicular to the orientation direction, the weaker intermolecular van der Waals forces predominate between the molecular chains, giving a much lower load-carrying capability. For amorphous polymers, an average orientation function defines the only measure required to define the orientation state completely; it relates directly to the load-carrying amorphous phase. In semicrystalline polymers, the Hermans orientation function (2) describes the orientation contribution by the crystalline phase. This must be combined with the amorphous-phase orientation to describe an average molecular orientation. Average orientation is more difficult to relate directly to physical properties because the crystalline phase does not contribute greatly to the load-bearing capabilities of the structure. Therefore, a more detailed analysis of the semicrystalline materials is required to determine the contributions from the amorphous and crystalline phases (25). Advanced analytical techniques are needed that are not readily available to many workers.

Biaxial Orientation. Biaxial orientation substantially improves the physical properties of the film and increases its commercial value. Biaxially oriented films are produced by stretching polymers in directions perpendicular to each other in the melt or rubbery state. The improvement over uniaxially oriented films is due to the redistribution of c-axis chain orientation (27). This results in a film with enhanced physical properties in both directions. The direction perpendicular to the machine direction is defined as the transverse (TD) direction.

Commercial biaxially oriented films are produced by the tenter-frame (Fig. 10), double-bubble (Fig. 11), or blown-film process (Fig. 12). In the tenter-frame and double-bubble processes, the polymer is stretched in the solid state below the crystalline melting point. In the blown-film process, the polymer is oriented in the melt followed by rapid quenching to immobilize the orientation (see ORIENTATION PROCESS).

The theoretical descriptions of biaxial orientation and the relationships to physical properties are not as well developed as those of uniaxial orientation. In amorphous polymers, birefringence can measure total molecular orientation and can be used to predict properties. For semicrystalline polymers, a more detailed description of the orientation is required before prediction of properties is possible.
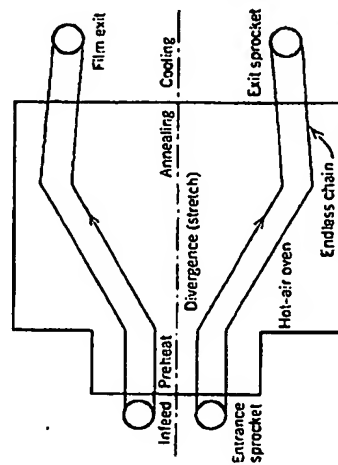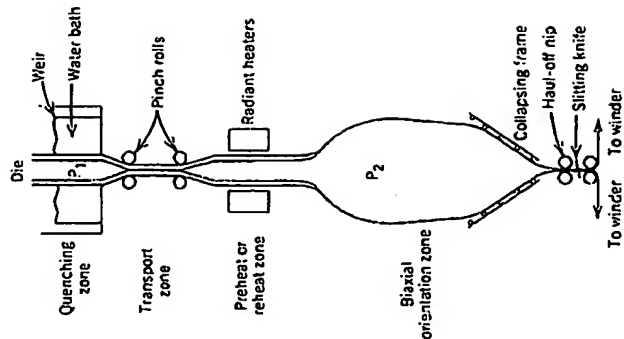

Fig. 10. Tenter orientation.

Fig. 11. Double-bubble orientation.

Average-orientation, amorphous-orientation, and crystalline-orientation functions are required to describe the oriented state completely (2,27). This description permits the calculation of amorphous-phase orientation, which is required to relate and predict physical properties. The determination of crystalline orientation requires the more advanced analytical techniques of x-ray diffraction or dichroic ratios from polarized ir spectroscopy. Average- or total-orientation functions are measured by birefringence. Amorphous- and crystalline-orientation functions are separated by measuring the sonic modulus and assuming a molecular model for the semicrystalline polymer (2).

Tenter-frame Process. Tenter frames (Fig. 10) consist of two side-by-side endless chains that diverge at a constant angle. The divergence of the chains forces the polymer to stretch as it is transported along the chain, and imparts the desired orientation. Stretch rate is determined by the chain speed, divergence angle, and extent of orientation. The extent of orientation is determined by the ratio of the width of the film entering to the width of the film leaving the system. Tenter systems have been developed primarily to impart TD orientation. Specialized systems allow simultaneous MD and TD stretching, but usually only TD orientation is carried out. The tenter frame, as part of a larger, sequential, biaxial-orientation system, can be located before or after MD orientation; it is usually located after MD orientation.
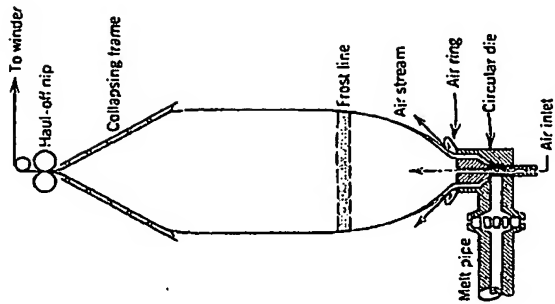
Fig. 12. Melt orientation.

The resin is extruded or coextruded as a flat sheet ca 0.75 mm thick onto a large chill roll in a quench bath. The cast sheet is reheated and stretched in the longitudinal direction on a series of heated chrome rolls and fed into a tenter chain equipped with clips to grip the film.

The chain system is located within a heat-transfer oven, where the sheet is heated to the temperature at which it is to be stretched. Heating is critical because the reliability of the stretching process and the film properties depend upon the temperature, stretch rate, and stretch ratio.

After preheating, the film is drawn in the transverse or cross direction by the divergence of the tenter chains, annealed, and released. The web is usually split into two smaller webs, which are treated by electric discharge for enhancing printability and wound into rolls.

In contrast to the double-bubble process, the tenter-frame process permits the direct manufacture of a film with improved dimensional stability because it is heat-set by adding a length of chain after the divergent section at the finished film width. This is very important for applications requiring good registration, as in printing or photographic applications. The film can be heated or cooled to a specific temperature while being restrained by the chain system. Production rate and speed are high; heat transfer rates must also be high to control crystallization.

After biaxial orientation, film properties can be enhanced by additional MD orientation. This step, called tensilizing, is performed by MD drawing of the film

between two rollers, as previously discussed. A typical tensilized process consists of the casting step, the MD-orientation step, the TD-orientation step, and another MD-orientation or tensilizing step.

The economics of the process are given in Table 3.

Table 3. Economics of a Tenter-frame Process[a]

Costs	Value
Operating costs, ¢/kg	
polymer	94.6
direct labor	22.0
depreciation	37.4
maintenance	22.0
utilities	22.0
administration and others	13.0
Total	*211.0*
Capital costs, $10⁶	
two 3-m orienters	17.1
four 3-m slitters	3.6
resin and reclaim	6.0
handling and storage	8.0
maintenance, quality control, others	6.5
land, buildings, utilities	20.8
Total	*59.00*
Capital cost per kg, $	*5.00*

[a] Plant capacity for film 18.75 μm thick, 11.8×10^3 t.

Blown-film Processes. Bubble-orientation technology permits simultaneous biaxial orientation directly from the melt (20) or by inflation of a quenched tube. With homogeneous films, the latter method may give films of slightly different properties than those of films produced on tenter frames. Melt orientation is less effective and properties are different because of lower orientation.

In the double-bubble method (Fig. 11), the resin is extruded as a tube that is quenched and gauged in cold water. The tube is then reheated and oriented by blowing it into a bubble. Simultaneously, the speed of the takeoff roll is increased for MD orientation; temperature is controlled by radiant electrical heaters. The bubble is collapsed, passed through nip rolls, reinflated, annealed in a controlled-temperature chamber, and collapsed again. After trimming the edges, it is separated into two webs, which are then treated by electric discharge for printability and wound into rolls.

The economics of the process are given in Table 4. The tenter-frame process has a cost advantage over the blown process at film gauges >18.75 μm, whereas the blown process has a cost advantage at film gauges <18.75 μm.

In melt orientation, the polymer melt is extruded from an annular die into a tube, which is simultaneously pulled away from the die as air is blown into the tube and around the outer surface (by an air ring attached to the die) to stabilize and quench the tube (20). This cools the melt as it accelerates in the machine in the radial direction, thus conferring orientation. The action of the air solidifies the melt. This point is called the frost line; it is important in de-

Table 4. Economics of Blown-film Processes

Costs	Large blown line[a]	Small blown line[b]
Operating costs, ¢/kg		
polymer	95	95
direct labor	22	46
maintenance	20	40
utilities	26	22
administration and others	13	13
depreciation	31	37
Total	207	255
Capital costs, $10⁶		
two 3.5-m orienters	12.0	
15 small blown lines		18.0
four 3.5-m slitters	4.2	
12 1.2-m slitters		5.8
resin and reclaim	6.0	6.0
handling and storage	6.6	6.6
maintenance, quality control, others	5.9	3.5
land, buildings, utilities	22.8	12.0
Total	57.5	51.9
Capital costs per kg, $	4.86	4.49

[a] Plant capacity for film 18.75 μm thick, 11.8 × 10³ t.
[b] Plant capacity for film 18.75 μm thick, 11.5 × 10³ t.

termining the reliability of the process and the film properties. Above the frost line, the inflated tube is gradually collapsed and fed to the haul-off nip, which supplies the power to pull the melt from the die and prevents the bubble from collapsing by trapping air in the tube. The MD orientation is determined by the speed at which the melt is pulled away from the die (haul-off rate), the quenching rate (frost-line height), the die gap, and the melt properties. The TD orientation is determined by the final diameter of the inflated tube in relationship to the die diameter (blow-up ratio). The ratio of the die gap to the film thickness is called the drawdown ratio. It affects the stability of the process and the orientation of the product. The tension pulling the melt away from the die (20) is called the haul-off tension. It cannot exceed the melt strength or the critical stress for melt fracture. The haul-off tension affects process stability and film properties.

Solvent–Solution Casting

Films and sheets may be made from polymers that cannot be melt-extruded or that require little heat by using polymer solutions. In this technology, a homogeneous polymer solution is filtered and degassed, followed by formation and drying of a gel film. The gels are formed from the solutions by evaporation and coagulation. Drying of the gels into self-supporting films is the rate-limiting step because it is diffusion-rate controlled. This also is of prime consideration in the formation of thick films, where drying times may be excessive. Consequently, these methods are generally limited to thin films. The characteristics of these films are low residual orientation, uniform properties in all directions, and excellent surface finishes (12,13).

Coagulation. Gel formation by coagulation depends upon the differential solubility of polymers in a blend of solvent and nonsolvent and solubility changes resulting from concentration changes of added chemicals. For example, solvents A and B are a good solvent and poor or nonsolvent, respectively, for polymer Y. A solution of Y is prepared in A and extruded into a bath of solvent mixture of A and B. The concentration difference causes diffusion of A into the bath and the diffusion of B into the polymer solution. As the concentration of B increases and that of A decreases, the polymer becomes less soluble and eventually precipitates as insoluble gel; complete evaporation of A and B leaves the finished film. Changes of pH may be sufficient to reverse the solubility or change the chemical nature of a polymer in solution, transforming it into an insoluble, stable gel. A good example of this technology is the casting of cellophane (13) (Fig. 13).
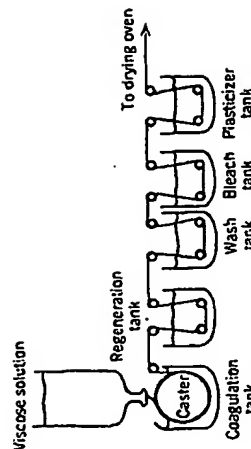

Fig. 13.   Cellophane casting process.

Evaporation. In this method (Fig. 14), the polymer solution is pumped through a die, cast upon a stainless-steel belt, and transferred to a drying chamber to evaporate; the solvent is recovered (13). As the solvent evaporates, a gel forms. Further drying gives a stable film. The film is stripped from the belt and rolled up.
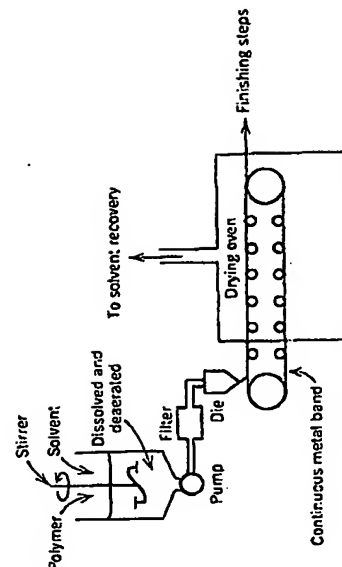

Fig. 14.   Solvent casting process.

Rolling

Rolling produces a film with predominately MD orientation by accelerating the film from a nip point where the thickness is reduced. Large forces are found at the nip point, but overall orientation can be increased over other forms of MD orientation. Plastic strapping is oriented by this method.

Calendering

Calendering (qv) produces an unoriented cast sheet with uniform gauge at high throughput (28,29). The equipment (Fig. 15) is expensive and consists of a stack of specially hardened, driven rolls. The rolls are often supported in such a manner that they may be bent or skewed relative to one another during operation. This operation is required to maintain uniform thickness by overcoming the forces developed in the calender nip. The high separating forces, ie, 180–1080 kg/cm of roll face, are generated by the melt (stack) viscosity and elasticity as the material passes through the nip point.
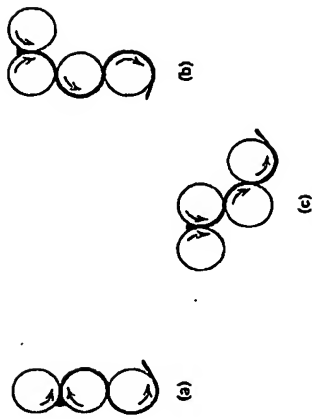

Fig. 15. Calendering-roll configurations: (a) three-roll superimposed type; (b) four-roll inverted-L type; (c) four-roll Z type.

Calenders are usually composed of four rolls that form three nips: feed nip, metering nip, and finishing nip. The polymer is supplied to the feed nip from a compounding operation and further mixed and heated by the circulating melt bank formed at the feed nip. Alternatively, a melt of partially fluxed compound may be supplied to the calender from an extruder or Banbury. The sheet is reduced at the metering nip to the final desired thickness. The gauge is adjusted at the finishing nip by bending the last roll or skewing the middle or third roll.

Finishing Operations

Coating. Films are coated by metering a solution onto the surface and removing excess solvent; the coatings are cured. For metering, airknife coaters, Meyer rod coaters, and direct or indirect gravure coaters (Fig. 16) are used. The
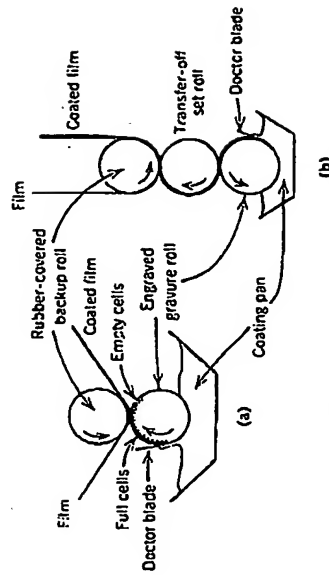
Fig. 16. (a) Direct and (b) indirect gravure systems.

film is unwound onto the coater and may require surface treatment to ensure proper wet-out, especially with water-based coatings. The film is coated at the coating station and transferred to a drying oven. After drying, the film is rewound and ready for further processing (see also COATING METHODS).

Embossing. Embossing is used to modify the film texture or decorate the film with a three-dimensional pattern (12). The film is heated to the softening point and distorted by passing it between a cooled roll with the three-dimensional pattern and a nip. This immobilizes the distorted pattern imposed by the embossing roll. The degree of distortion depends upon the film properties and the processing conditions.

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H. C. PARK
E. M. MOUNT III
Mobil Chemical Company

FILMS, MULTILAYER

Multilayer coextrusion of thermoplastic film and sheet began only twenty years ago and has developed into an important plastic fabrication process, providing large growth opportunities for the plastics industry. Coextruded multilayer plastics are challenging such traditional materials as metals, glass, paper, and textiles.

The attraction of coextrusion is both economic and technical. It is a single-step process starting with two or more plastic materials that are simultaneously extruded and shaped in a single die to form a multilayer sheet or film. Thus, coextrusion avoids the costs and complexities of conventional multistep lamination and coating processes, where individual plies must be made separately, primed, coated, and laminated. Coextrusion readily allows manufacture of products with layers thinner than can be made and handled as an individual ply. Consequently, only the necessary thickness of a high performance polymer is used to meet a particular specification of the product. In fact, coextrusion has been used commercially to manufacture unique films consisting of hundreds of layers with individual layer thicknesses less than 100 nm (1). It is difficult to imagine another practical method of manufacturing these microlayer structures.

Layers may be used to place colors, bury recycle, screen ultraviolet (uv) radiation, minimize die-face buildup, and to control film-surface properties. Additives, such as antiblock, antislip, and antistatic agents, can be placed in specific layer positions. High melt strength layers can carry low melt strength materials during fabrication.

The largest market for coextruded films and sheets is in packaging applications, eg, two- or three-layer films for trash bags or five-to-nine-layer structures for flexible and semirigid packages. As many as five different polymers may be used to obtain heat sealability, barrier, chemical resistance, toughness, formability, and aesthetics. Coextrusion is also suitable for applying thin multilayer films as coatings on substrates (2). Growing applications for coextrusion are in automotive, construction, appliance, sanitaryware, and recreational vehicle markets.

This article summarizes coextrusion technology, including coextrusion dies, polymer specifications for coextrusion, recycling of multilayer scrap, and some commercial applications (see also FILMS; SHEETING).

Methods of Coextrusion

Coextruded films are produced by a tubular-blown film process and a flat-die, chill-roll casting process. Capital and operating costs for blown-film vs cast-film coextrusion lines are strongly dependent on product mix and utilization. Equipment suppliers provide comparative economic evaluations for specific products. Practical cast-film equipment has been discussed in a recent article (3). Coextrusion dies are unique. Extruders used before the die and take-away equipment used afterwards are standard equipment for single-layer film manufacture of blown or cast film (see EXTRUSION; FILMS, MANUFACTURE).

Tubular-blown Film Process. This process is more flexible with regard to the permissable polymer viscosity mismatch, control of film orientation balance in the transverse and machine directions through blow-up ratio, and easy randomization of film-thickness variations. Production rates are limited by flow rates per circumferential length of die (pressure drop) and cooling rates (heat transfer).

Casting Process. The flat-die, chill-roll, cast-film process is more suitable for high volume production on dedicated lines because of higher output rates obtained by wide dies and more efficient cooling on chill rolls. Cast films usually have better clarity than blown films because of rapid quenching, but uniaxial orientation can cause the film to split in the machine direction for some structures.

Coextrusion Dies

Tubular-blown Film Dies (Circular Dies)

Tubular coextrusion dies were the earliest dies used to make multilayer plastic film. Successful design requires formation of uniform concentric layers in the annular die land formed by the mandrel and adjustable or nonadjustable outer die ring. Early designs included center-fed dies that had the mandrel supported by a spider (4). Feedports arranged a concentric melt stream that was pierced by the mandrel as it flowed to the die exit, forming annular layers. Limitations of this early design were discontinuity and nonuniformity caused by spider-induced weld lines in the layers.

Another early design used stacks of toroidal distribution manifolds, so that